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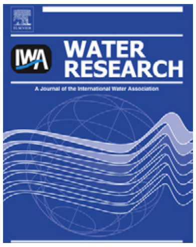

# Electrochemical sulfide removal from synthetic and real domestic wastewater at high current densities

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ABSTRACT

Hydrogen sulfide generation is the key cause of sewer pipe corrosion, one of the major issues in water infrastructure. Current abatement strategies typically involve addition of various types of chemicals to the wastewater, which incurs large operational costs. The transport, storage and application of these chemicals also constitute occupational and safety hazards. In this study, we investigated high rate electrochemical oxidation of sulfide at Ir/Ta mixed metal oxide (MMO) coated titanium electrodes as a means to remove sulfide from wastewater. Both synthetic and real wastewaters were used in the experiments. Electrochemical sulfide oxidation by means of indirect oxidation with in-situ produced oxygen appeared to be the main reaction mechanism at Ir/Ta MMO coated titanium electrodes. The maximum obtained sulfide removal rate was $11.8 \pm 1.7$ g S $m^{-2}$ projected anode surface $h^{-1}$ using domestic wastewater at sulfide concentrations of $\geq 30$ mg $L^{-1}$ or higher. The final products of the oxidation were sulfate, thiosulfate and elemental sulfur. Chloride and acetate concentrations did not entail differences in sulfide removal, nor were the latter two components affected by the electrochemical oxidation. Hence, the use of electrodes to generate oxygen in sewer systems may constitute a promising method for reagent-free removal of sulfide from wastewater.

## 1. Introduction

Hydrogen sulfide is ubiquitously found in domestic and industrial wastewaters (Dutta et al., 2008). It is a toxic, corrosive and odorous compound, often requiring removal from the aqueous or gaseous phase before discharge into the environment. Hydrogen sulfide is of particular concern in sewer systems since it causes corrosion of sewer pipes. Current technologies for sulfide abatement in sewer systems involve adding chemicals to wastewater to prevent sulfide formation, or its transformation from liquid to gas phase (WERF, 2007). The commonly used chemicals include oxidants such as oxygen (Gutierrez et al., 2008; Zhang et al., 2008) and nitrate (Hvitved-Jacobsen, 2002; Mohanakrishnan et al., 2009) for sulfide oxidation, iron salts for sulfide precipitation (Firer et al., 2008; Nielsen et al., 2008; Zhang et al., 2009) and magnesium hydroxide to elevate pH (Gutierrez et al., 2009; Zhang et al., 2008). Other chemicals used include chlorine, hydrogen peroxide, caustic and nitrite, which are toxic to sewer biofilms (Mohanakrishnan et al., 2008; Zhang et al., 2008). These strategies are considered expensive (\$1.7–7.2 kg S $removed^{-1}$) (Zhang et al., 2008) and often come with a number of limitations such as sludge generation or loss of organics, the latter are needed for nutrient removal in downstream WWTPs.

Recent advances in electrode development and operation have increased the interest in electrochemical abatement strategies. Electrochemical techniques offer several advantages including no requirement for dosing, transport and storage of

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hazardous chemicals, robustness, versatility, controllability and the amenability to automation (Ángela et al., 2009). A typical electrochemical reactor consists of an anode, a cathode and a membrane separating both. At the anode, electrochemical oxidation of a pollutant (here sulfide) can be achieved. Electrochemical oxidation can be achieved either by direct oxidation at the electrode surface or by indirect oxidation. During indirect electrochemical oxidation, oxidants including $OH^\bullet$, $O_2$ and $Cl_2$, are generated at the anode surface; these subsequently oxidize the pollutant in the bulk solution. The reaction mechanism and selectivity of the oxidation process are mainly determined by the electrode material, the flow regime and the applied anode potential. Thus, depending on the conditions, sulfide can be oxidized at the anode or oxidized by in-situ generated oxidants. Sulfide can be oxidized to elemental sulfur, thiosulfate or sulfate. The oxidation of sulfide to sulfur is preferable since this requires the least amount of electrons and thus energy input (Dutta et al., 2009).

A number of studies on aqueous electrochemical sulfide oxidation have been performed in the past (Ateya and Al-Kharafi, 2002; Ateya et al., 2007; Dutta et al., 2008, 2009, 2010; Farooque and Fahidy, 1978; Waterston et al., 2007). However, most of these studies reported on the direct oxidation of sulfide to elemental sulfur at carbon based anode materials using high strength/conductivity solutions such as alkaline media and brine solutions, at high sulfide concentrations and predominantly operated at low current densities (Ateya and Al-Kharafi, 2002; Ateya et al., 2007; Dutta et al., 2009; Farooque and Fahidy, 1978). However, for sewer systems, low current densities using high surface area carbon based electrodes are not feasible due to the large reactor size that would be required. Domestic wastewater typically has a sulfide content of around ~10 mg $HS^- L^{-1}$, which is much lower than the concentrations tested in the aforementioned studies (Nielsen et al., 2003). Furthermore, since the electrochemical cell has to treat raw unfiltered sewage, flat mesh shaped electrodes are needed to avoid blockage and ragging of the system. Taking into account the low sulfide concentration and the use of flat mesh shaped electrodes (low surface area) indirect electrochemical reactions are likely to play a dominant role due to the limited reactant availability at the electrode surface.

IrOx coated titanium electrodes are extensively used as oxygen evolution electrodes in electroflotation and electrocoagulation reactors (Chen, 2004). Miller and Chen (2005) reported on the direct anodic sulfide oxidation using titanium based $Ti/Ta_2O_5{-}IrO_2$ electrodes from a caustic medium. This implies that, depending on the operational conditions (e.g. anode potential, sulfide concentrations), simultaneous sulfide oxidation and in-situ oxygen generation should be achievable. This oxygen can be used as a downstream control measure by inhibiting either the activity of sulfate reducing bacteria (SRB) and/or the oxidation of the sulfide that has been produced (Gutierrez et al., 2008). The kinetics and stoichiometry of the oxidation of sulfide by oxygen is well described in literature (Kuhn et al., 1983; Nielsen et al., 2003).

Therefore, the aim of this study was to examine the feasibility of simultaneous oxidation of aqueous sulfide to elemental sulfur and water to oxygen at high current densities, using defined synthetic feed and domestic wastewater and an Ir/Ta MMO coated titanium electrode as anode.

## 2. Materials and methods

### 2.1. *Electrochemical cell and operation*

The two-chambered electrochemical cell consisted of two parallel Perspex frames (internal dimensions 14 × 12 × 2 cm) separated by a cation exchange membrane (Ultrex CM17000, Membranes International Inc., USA). In the anode chamber, a mesh shaped Ir/Ta MMO ($IrO_2/TaO_2$: 0.65/0.35) coated titanium electrode with a projected surface area of 100 $cm^2$ was used (Magneto Anodes BV, The Netherlands). Stainless steel fine mesh (168 $cm^2$) with a stainless steel current collector (6 mm mesh size, 0.8 mm wire) was used as electrode material in the cathode chamber. The anode liquid medium was constantly recirculated over an external buffer vessel, allowing a total anode liquid volume of 5 L. We operated the reactors in fed batch mode, as a once through system would have required cubic meter volumes of defined media/sewage per day to enable operation of the reactors at the desired current densities. The latter was not practical in the laboratory. The disadvantage of this recirculatory mode, however, is that the "influent" sulfide concentration into the reactor will slowly increase if 100% removal efficiency is not achieved. In the experiments, the sulfide concentrations increased from 30 to ~90 mg $L^{-1}$, depending on the current applied and anode medium used, as the experiments progressed. An example of the typical sulfide concentration profile during the course of the experiments is shown in Fig. 4.

The influent flow rate through the anode chamber was maintained at 15 L $h^{-1}$ using a peristaltic pump (Watson Marlow, UK). The off gas coming from the external buffer vessel was sent through a water-lock containing a 0.2 M NaOH solution. The recirculation flow in the anode chamber was kept at 22 L $h^{-1}$ using a peristaltic pump (Watson Marlow, UK) to obtain a higher mixing rate in the anode chamber. PVC tubing with an internal diameter of 4.5 mm was used for the feeding and recirculation lines.

In all experiments, an Ag/AgCl (RE-5B, Bio Analytical, USA) was used as the reference electrode. Its potential was estimated at +197 mV versus standard hydrogen electrode (SHE).

An external buffer flask of 2 L was used in the recirculation of the cathode chamber. A 0.1 M NaOH solution in the cathode chamber was used in all experiments to trap any possible crossover of hydrogen sulfide. The recirculation flow of the cathode solution was kept at 22 L $h^{-1}$ using a peristaltic pump (Watson Marlow, UK). Experiments were initially performed using a defined synthetic feed (with composition to be described later) and subsequently domestic wastewater. Both for the synthetic and real domestic wastewater experiments, sodium sulfide ($Na_2S\cdot 9H_2O$) was supplied continuously to the incoming line of the anode chamber via a syringe pump (NE-1600, New Era Pump Systems, Inc., USA) at a dosing rate of 149 ± 20 mg S $h^{-1}$, i.e. sufficient to give an anode influent concentration of ~10 mg S $L^{-1}$. Before use, $Na_2S\cdot 9H_2O$ crystals were washed with MilliQ (18 MΩ) water to remove oxidized sulfur species on the surface of the crystals (Dutta et al., 2008). Due to the production of protons at the anode, a decrease of the anode pH is expected over time. To compensate for this, $NaHCO_3^-$ was added (5 g $L^{-1}$) in the experiments using synthetic feed to maintain pH values